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COMBUSTION OF HYDROCARBONS IN AN ADIABATIC FLOW
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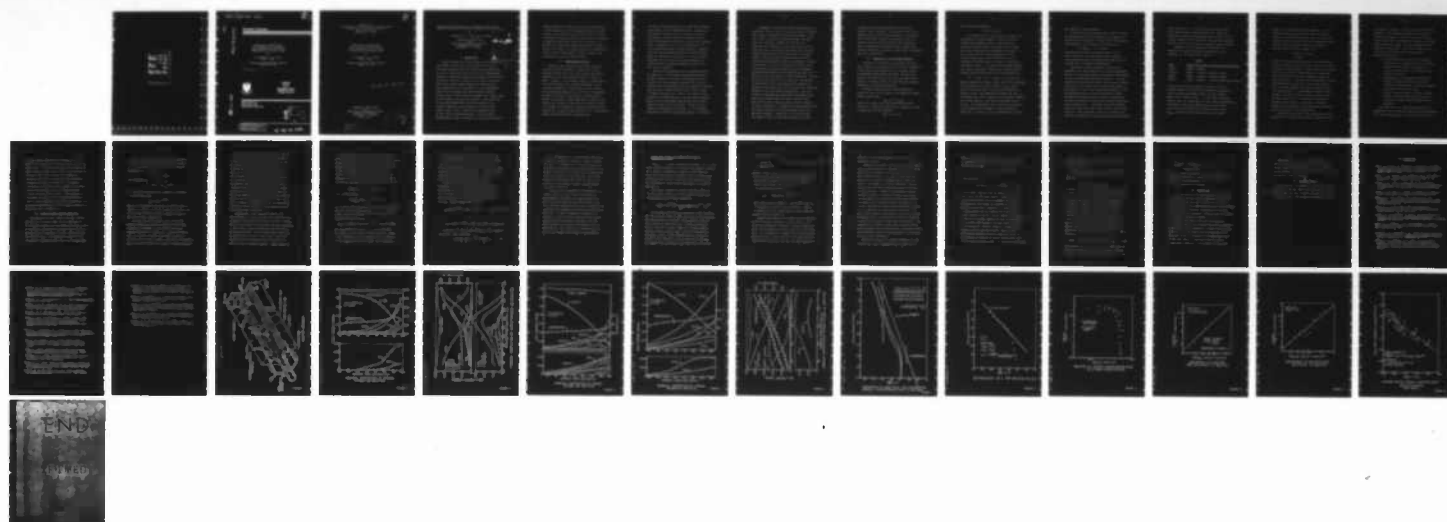
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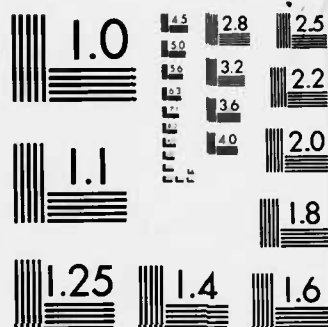
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Princeton University

Combustion of Hydrocarbons
in an Adiabatic Flow Reactor:
Some Considerations and Overall
Correlations of Reaction Rate

by

I. Glassman, F. L. Dryer
and R. Cohen

Aerospace and Mechanical Sciences
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I. Introduction

Recent concerns about energy needs and the associated environmental problems has again focused attention on the rather startling fact that after burning hydrocarbons for about a century we still do not have a thorough understanding of their high temperature oxidation characteristics. The central thrust of a program at Princeton on the homogeneous gas phase reaction kinetics of hydrocarbons at high temperatures is to contribute to this understanding. Earlier work on methane and carbon monoxide oxidation kinetics [Dryer, 1972; Dryer and Glassman, 1973; Dryer, Naegeli and Glassman 1971] has been reported in the literature. All the experimental work had been performed on the Princeton adiabatic, high temperature, turbulent-flow reactor (Dryer, 1972). Some recent experimental work on this reactor, albeit preliminary, and some further understanding of what is necessary to model complex chemical



kinetic systems are thought to be of great significance in further elucidating the hydrocarbon oxidation kinetic process. More specifically this work which is reported here deals with some preliminary thinking on the processes in paraffin hydrocarbon combustion; the issue of induction and steady state oxidation kinetics; the use of global, semi-global, or overall reaction rate expressions; and some detail measurements on ethane oxidation that lends credence to the concepts exposed.

II. Experimental Apparatus

Basically, the Princeton flow reactor technique utilizes a heated cylindrical quartz duct 10 cm in diameter through which a hot inert carrier gas flows at velocities which yield Reynolds numbers in excess of 3500. (Figure 1). The reactor assembly is constructed so that the reactor walls rapidly equilibrate to the local gas temperature. Rapid mixing of small amounts of pre-vaporized reactants with the carrier is provided by radial injection at the throat of a high velocity mixing inlet nozzle. Proper adjustment of carrier temperature flow velocity and reactant concentrations result in a steady, one dimensional, adiabatic reaction zone extending over a length of approximately 85 cm. Simultaneous thermal and chemical data at discreet axial

locations in the reaction zone are obtained by longitudinal extension of an instrumented probe. Temperature measurements are made with a silica coated Pt/Pt-Rh thermocouple, and gas samples are removed through a water-cooled/expansion quenched stainless steel sampling probe. Consistent with the long range objective of more complex hydrocarbon oxidation studies, a sophisticated gas chromatographic chemical analysis procedure which was developed by Colket et. al. (1973), permits measurements of all stable hydrocarbon species (including partially oxidized compounds) as well as H_2 and O_2 to 1% precision.

Several unique advantages of this approach should be emphasized. By restricting experiments to highly diluted mixtures of reactants, and extending the reactions over large distances, gradients are such that diffusion may be neglected relative to convective effects; thus the measured specie profiles are a direct result of chemical kinetics only. This is in contrast to low pressure one dimensional burner studies where diffusion effects must be determined analytically before useful chemical kinetic data are obtained. While this procedure has progressed significantly in its refinement, estimation of diffusive corrections remain very difficult.

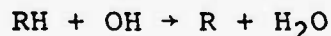
Furthermore, in the flow reactor uniform turbulence results not only in rapid mixing of the initial reactants, but radially 1-dimensional flow characteristics. Thus real "time" is related to distance through the simple plug flow relations. However, the relation of a specific axial coordinate to real time is not well defined since the initial time coordinate occurs at some unknown location within the mixing region. One would suspect that initial mixing history might therefore alter reaction phenomenon occurring downstream. However, the existence of very fast elementary kinetics, which initiate chemical reaction before mixing is complete, permit rapid adjustment of the chemistry to local conditions as the flow approaches radial uniformity. Furthermore, the large dilution of the reactants and rapidity of the kinetics reduce the coupling of turbulence and chemistry to the point that local kinetics are functionally related to the local mean flow properties. This conclusion is experimentally supported by excellent agreement of the derived chemical kinetic data with that obtained from shock tubes and static reaction systems at other temperatures. Agreement also substantiates that the reactor surfaces do not significantly effect the gas phase kinetics. Comparison of flow reactor data from reactor tubes of significantly different surface

to volume ratio also corroborates this conclusion. Finally and most important, the turbulent flow reactor approach permits kinetics measurements in a temperature range (800-1400K) generally inaccessible to low temperature methods (fast flow Electron Spin Resonance, Kinetic Spectroscopy techniques, static reactors etc.) and high temperature techniques (shock tubes, low pressure post flame experiments).

III. Combustion of Paraffin Hydrocarbons

Combustion of paraffins above methane has always been thought to be complicated by the greater instability of the higher alkyl radicals and by the great variety of secondary products which can form. The oxidation mechanism characteristically follows the Semenov type. Minkoff and Tipper (1962) have reported some oxidation mechanisms of specific hydrocarbons.

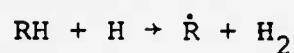
At higher temperatures most have accepted the primary reaction in the system to be between the hydroxyl radical and the fuel.



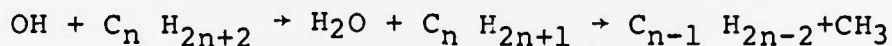
Recent work (Dryer, 1972) has suggested that other reactions in addition to this one were important; namely, in fuel lean and rich combustion



and in fuel rich combustion



It is interesting to review a general pattern for the oxidation of hydrocarbons in flames as given by Fristrom and Westenberg (1965). They suggest two essentially thermal zones: the primary zone in which the initial hydrocarbons are attacked and reduced to CO, H₂, H₂O, and the various radicals (H, O, OH) and the secondary zone in which the CO and H₂ are oxidized. The primary zone, of course, is where the intermediates occur. In oxygen-rich saturated hydrocarbon flames, they suggest further that initially hydrocarbons lower than the initial fuel form according to



Because hydrocarbon radicals higher than ethyl are thought to be unstable, the initial radical C_n H_{2n+1} usually splits off CH₃ and forms the next lower olefinic compound as shown. With hydrocarbons higher than C₃H₈, it is thought there may be fission into an olefinic compound and a lower radical. The radical alternately splits off CH₃. The formaldehyde which forms in the oxidation of the fuel and fuel radicals is rapidly attacked in flames by O, H, and OH, so that formaldehyde is usually

only found as a trace substance.

In fuel-rich saturated hydrocarbon flames, Fristrom and Westenberg state the situation is more complex, although the initial reaction is simply the H atom abstraction analogous to the preceding OH reaction: e.g.



Under these conditions the concentration of H and other radicals is large enough that their recombination becomes important and hydrocarbons higher than the original fuel are formed as intermediates.

The general features suggested by Fristrom and Westenberg have been confirmed in our recent experiments. However, this new work permits more detailed understanding of the high temperature oxidation mechanism. As stated earlier this work shows that under oxygen-rich conditions initial attack by O atoms must be considered as well as the primary OH attack. More importantly however, it has been established that the paraffin reactants produce intermediate products which are primarily olefinic and the fuel is consumed to a major extent before significant energy release occurs. The higher the initial temperature the greater the energy release as the fuel is being converted. This observation leads one to conclude that the olefin oxidation rate simply increases more appreciably

with temperature; i.e., the olefins are being oxidized while they are being formed from the fuel. These conclusions are based on recent experimental results as typified by Figures 2-6 which represent the data taken throughout the reaction zone of ethane, propane, butane and hexane.

A summary of the intermediates formed from the oxidation of these four paraffin hydrocarbons is most revealing and is represented by Table I.

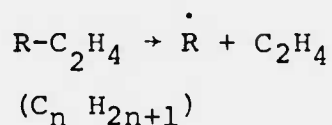
Table I

<u>Fuel</u>	<u>Relative Hydrocarbon Intermediate Concentrations</u>
ethane	ethene >> methane
propane	ethene > propene >> methane > ethane
butane	ethene > propene >> methane > ethane
hexane	ethene > propene > butene > methane >> pentene > ethane

It would appear that the results in Table I would contradict elements of Fristrom and Westenberg's suggestion that the initial hydrocarbon radical $C_n H_{2n+1}$ usually splits off the methyl radical. If this type of splitting were to occur, one could expect to find larger concentrations of methane. The large concentrations of ethene found in all cases would suggest that primarily the initial $C_n H_{2n+1}$ radical cleaves between the second and third

carbon to give ethene plus another radical. If one assumes the abstraction process to give the initial radical is from the second carbon atom as in lower temperature oxidation process, then the formation of ethene from this type of cleavage appears quite logical.

Thus the new reaction step appears to be



Notice the relative concentrations of propene found in butane and hexane oxidation and that very little pentane is found in hexane oxidation. These results would suggest that next to cleavage between second and third carbon atoms, the next most important cleavage is after the third carbon atom. Contrary to the suggestion of Fristrom and Westenberg, splitting off of the methyl radical, that is cleavage between the first and second carbon, is least important. In iso-compounds, cleavage would probably take place between the tertiary carbon atom and the one next to it. The dominant olefin would probably not be ethene. In the case of 2-methyl-pentane one could postulate that propene>butene>ethene must be the order of the intermediates.

Figures 2-5 show clearly that experimentally there appears to be an initial iso-energetic step in the over-

all process. Of course, this step is not exactly iso-energetic. The conversion process from paraffin to olefin is endothermic; however, some of the hydrogen formed during what is essentially a pyrolysis step does react and release energy. The two reactions are compensating energetically. Thus, the evidence is that there are three distinct, but coupled zones, in hydrocarbon combustion.

- 1) Following ignition, primary fuel disappears with little or no energy release and produces unsaturated hydrocarbons and hydrogen. A little of the hydrogen is concurrently being oxidized to water.
- 2) Subsequently, the unsaturated compounds are further oxidized to carbon monoxide and hydrogen. Simultaneously the hydrogen present and formed is oxidized to water.
- 3) Lastly, the large amount of carbon monoxide formed is oxidized carbon dioxide and most of the heat release from the primary fuel is obtained.

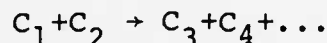
Each zone must have a different temperature dependency and thus at different temperatures the importance of a given step may change. Again on the basis of some

very preliminary experimental evidence as given by Figure 6 it is possible to put forth some interesting speculations. The initial condition of the experiment whose results are depicted in Figure 6 was such that not only was it more fuel rich than the examples of Figures 2-5 but also at a higher initial temperature. Examination of Figure 6 reveals that the maximum concentration of ethene is found earlier in the system. Essentially this means that the exothermic ethene oxidation step has become faster. This conclusion is supported by the fact that the temperature profile in Figure 6 rises continually and does not appear flat (iso-energetic) throughout most of the process as found for the conditions given in Figures 2-5.

IV. Current Chemical Kinetic Modelling

The concept of overall (global) reaction kinetics and its use is a direct result of the complexity of most chemical reactions and the complicated fluid mechanical situation in which some knowledge of heat release or chemical rates is necessary (ram jets, rocket engines, gas turbines, etc.). The assumption invoked is that the course of chemical kinetic events may be described

in terms of a few of the main reactants and products (C_i) in a functional relation with much of the same form as an elementary reaction process. Typically, the equation is of the form:



with rate given by

$$-[\dot{C}_1] = k_{ov} \prod_{i=1}^m [C_i]^{n_i}$$

k_{ov} , the overall specific rate constant, is expressed in the Arrhenius form

$$k_{ov} = 10^A e^{-E/RT}$$

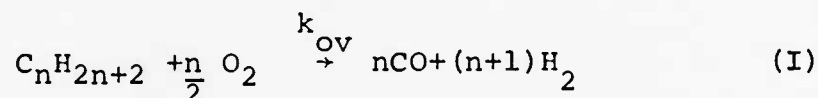
The n_i 's are defined as the orders of reaction with respect to C_i , and $\sum n_i$ is termed the overall reaction order. 10^A and E are termed the overall frequency factor and activation energy respectively.

The relation implies nothing about the actual kinetic mechanism (in terms of elementary reactions), although the parameters in the strictly empirical relation sometimes are governed by a single elementary step (or a number of steps) which basically control the rate of the chemical process. Under what circumstances such an overall correlation is usable is largely dependent

on both the kinetic mechanism to which it is applied and the physical environment in which the process is occurring. Levy and Weinberg (1959) concluded that the approximation is not generally applicable to chemical measurements taken in flames; however, this fact may not arise from the chemistry itself, but from the physical structure and diffusive character of the flames studied. Where a particular rate-determining step or sequence in the true chemical reaction mechanism occurs and the physical circumstances of the application are similar to those in which the expression was derived, the overall approximation is a valid and vastly simplifying idea. However, extension of such a correlation to experimental conditions outside the range studied should never be done without some reservation.

Considerable global modelling efforts have been attempted for carbon monoxide and these have been reviewed by Dryer (1972) and Howard et.al. (1973). Methane ignition and oxidation kinetics have also been expressed in this manner, often in conjunction with developing detailed mechanisms. Many of these studies were also reviewed by Dryer (1972). Avery (1953) is the only research which has attempted global modelling of a higher paraffin oxidation (Butane). Global modelling

has the potential to describe only spatial energy release and reactant/final product concentrations. However, prediction of more detailed parameters such as intermediate species is not possible. Edelman and Fortune (1969) have proposed a "quasi-global" modelling procedure for paraffin hydrocarbons as an approach to supplying these details. This technique approximates the paraffin hydrocarbon oxidation as a global reaction,



with a rate given by

$$- \frac{d[C_nH_{2n+2}]}{dt} = [C_nH_{2n+2}]^a [O_2]^b k_{ov} \quad (II)$$

and combines these expressions with a number of elementary reactions from the hydrogen/oxygen and carbon monoxide/oxygen reaction mechanisms. Values for a and b were assigned (a=0.5, b=1) and k_{ov} ,

$$k_{ov} = 1.8 \times 10^9 [(T/1111) - 0.5] T^{0.5} P^{0.2} \exp[-13,700/RT]$$

was determined from results of an analytical study of propane ignition kinetics (Chintz and Bauer, 1965). It was suggested that this mechanism could be applied in the temperature range 800-3000K. The assumption

that a quasi-global model based on propane characteristics was applicable to higher paraffins was presumed to be substantiated by shock tube ignition delay experiments performed by Nixon et. al. (1964-1967). These experiments identified some similarity in the functional behavior and the order of magnitude of ignition delay times for propane/and n-octane/oxygen mixtures.

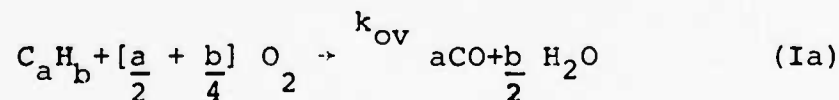
The quasi-global model thus developed has undergone some revision, as more ignition delay and elementary reaction data became available, primarily in the values of elementary rate constants for hydrogen-oxygen and CO-oxygen reactions and the expression for k_{OV} . Recent applications quote k_{OV} as

$$k_{OV} = 6 \times 10^9 P^{-0.815} T \exp[-12,200/RT], \quad \text{Edelman et.al. (1972)}$$

or

$$k_{OV} = 5.52 \times 10^8 P^{-0.825} T \exp[-12,200/RT], \quad \text{Engleman et.al. (1973)}$$

In accordance with earlier work (Marteney, 1970), Hammond and Mellor (1971) suggested



to replace expression (I) in preliminary analytical studies of gas turbine emissions. However, Bowman, in comments to Edelman et.al. (1972) has shown that "infinite" quasi-global kinetics do not offer any significant advantages over the partial equilibrium approach to prediction of NO_x emissions, and he concluded that these approaches were far inferior to detailed or quasi-global kinetics interpretations of methane oxidation.

It should be re-emphasized that Engleman et. al. (1973) is the only study which has attempted to experimentally corroborate the Edelman model with other than shock tube ignition delay results, and this study was restricted primarily to a comparison of experimentally measured and analytically predicted NO_x emissions. No other fundamental experimental information to which the semi-global equation might be compared has been available previously, and thus there has been no challenge or corroboration of its applicability. The studies to be reported here are the first to supply some insight to this question.

V. Global Modelling of the Hydrocarbon Systems - Particularly Ethane.

Clearly a new global mechanism is needed for the initial olefin formation phases of the hydrocarbon oxidation process. The oxidation of methane was studied in some detail by Dryer (1972) and Dryer and Glassman (1973), and encouraged the belief that the rate of reaction of hydrocarbon could be expressed by a simple global expression of the form of Equation II.

The rate of reaction in the post induction phase of the lean methane oxidation was experimentally found to be well described by the overall expression

$$-\dot{[CH_4]} = 10^{13.2 \pm 0.2} \exp \left(\frac{-48,400 \pm 1200}{RT} \right) [CH_4]^{0.7} [O_2]^{0.8}$$

It should be noted that the parameters of this equation are significantly different than those found by investigators who have studied the induction (ignition delay) phase of this reaction in shock tubes [e.g. Skinner & Ruehrwein (1959), Asaba et.al. (1963), Higgin and Williams (1969)] and flow reactors [Lloyd (1946), Mullins (1953), Nemeth and Sawyer (1969)]. These studies predicted the rate of reaction to be inhibited by the concentration of methane. For example Seery and Bowman (1970) empirically correlated

the ignition delay time as

$$\frac{1}{\text{Reaction Rate}} \propto \tau = 7.65 \times 10^{-18} \exp[51,400/RT] [\text{CH}_4]^{0.4} [\text{O}_2]^{-1.6}$$

However, Figure 7 shows a comparison of the overall rate constant derived by Dryer (1972) with results calculated from parameters predicted by the detailed analytical studies after Bowman (1970). An analytical overall rate constant was calculated from

$$k_{\text{ov}} = - [\dot{\text{CH}}_4] / ([\text{CH}_4]^{0.7} [\text{O}_2]^{0.8})$$

Clearly there are two phases of this reaction which are not modelled by the same global parameters. Indeed, the experimental flow reactor data of Dryer (1972) show similar behavior (Figure 8).

Qualitative comparison of ignition delay characteristics of propane (Hawthorne & Nixon, 1966) and the rate of disappearance of propane in the post induction phase of its oxidation (Figure 3) are also in disagreement. It is important to remember that the semi-global modelling effort reviewed earlier was derived primarily from ignition delay data, and yet this model purports to

describe finite disappearance rates of fuel during the combustion process.

Indeed, the induction (ignition) phase of the hydrocarbon oxidation with the exception of fuel rich methane combustion is generally very short relative to the post induction reaction. In fact, in some practical situations, the ignition kinetics may be totally precluded. For example, in turbine combustors, recirculation of hot, partially burned gases provides stabilization of the combustion. These hot gases contain partially oxidized reactants, combustion products, and some reactive centers, all of which may significantly effect the initial chain branching mechanism leading to ignition. Thus partial stirring may significantly reduce or even eliminate the ignition phase chemistry. The post induction phase of the reaction will remain largely unaffected, and it is this chemistry which is important to prediction of energy release rate and emissions. The turbulent flow reactor is particularly suited to study of this phase of the reaction and can in addition provide some information about ignition chemistry in cases where it must also be considered.

Furthermore Equation II appears inadequate for describing the rate of disappearance of initial fuel in

higher paraffin oxidation reactions. If one conducts an experiment at constant temperature and large concentrations of oxygen, Equation II would predict

$$-(C_n H_{2n+2}) = \text{Constant } (C_n H_{2n+2})^a$$

Thus a plot of

$$\log (C_n H_{2n+2}) \text{ vs. } \log (C_n H_{2n+2})$$

should yield a straight line of slope a. Figure 9 is such a plot of flow reactor data on ethane oxidation. The non-linearity of the curve suggests that ethane disappearance rate cannot be described by a functional relation of the form of Equation II. Similar behavior is also observed for the oxidation of propane and butane (Figures 3 and 4). Thus it appears that Equation II does not in general predict the rate of disappearance of a paraffin hydrocarbon in the post induction phase of its oxidation. Further, Figure 2 as discussed previously suggests that the paraffin reactant produces intermediate products which are primarily olefins and the paraffin is consumed to a major extent before significant energy release occurs. If the kinetics followed

a mechanism represented by Equation I, there would be considerable energy release proportional to initial reactant disappearance.

In contrast, the following correlation was found to give a good representation of some extensive data taken with ethane:

$$-[\dot{C}_2H_6] \sim ([C_2H_6]_0 - [C_2H_6])^a$$

An example of how well these data fit this correlation is given in Fig. 10 for the experimental data shown in Fig. 2. For nine/ethane/air runs the average value of the slope, determined by the least-squares method, is $a=0.975 \pm 0.05$. There is, however, a small temperature rise in each run which contributes to the slope.

Taking the temperature rise into account, the fuel dependence is reduced to the 0.80 ± 0.03 power of the amount of ethane reacted (Fig. 11) and the activation energy is about 33 kcal/mole. Experiments were then made in which the initial oxygen concentrations and equivalence ratios were varied ($6.06 < \phi < 0.79$). A global correlation of the form

$$-[\dot{C}_2H_6] = k_E ([C_2H_6]_0 - [C_2H_6])^{0.8} [C_2H_6]^b [O_2]^c \quad (III)$$

was attempted for all the data. It was found that "b" could not be defined and "c" was negligibly different from zero. The final correlation (Figure 12) was found

to be

$$-[\dot{\text{C}}_2\text{H}_6] = 10^{7.18 \pm 0.33} \exp[(-32,900 \pm 1530)/RT] \quad (\text{IV})$$

$$[(\text{C}_2\text{H}_6)_0 - (\text{C}_2\text{H}_6)]^{0.8}$$

As yet, no detailed mechanism has been developed to explain this correlation. However, similar correlations also have been qualitatively recognized for propane and butane-oxygen rich reactions.

VI. Conclusions

The applicability of kinetic measurements obtained in induction (ignition) phase measurements such as those made in shock tube and those obtained in the post induction phase by flow reactors has been clearly delineated - particularly with reference to hydrocarbon oxidation. The usefulness and limitation of global kinetic modelling has also been carefully analyzed.

Experimental results show that there appears to be three stages in the paraffin hydrocarbon oxidation process that must be considered if there is to be global modelling. The new element is a well defined initial step most easily recognizable in the temperature range of the flow reactor. This step is the relatively isoenergetic conversion of the paraffin to the olefin.

Extensive work with ethane indicates that the conversion rate is proportional to the amount of ethane converted. Future work will attempt to explain this functional dependence of this phase of the overall paraffin hydrocarbon oxidation process.

VII. Acknowledgement

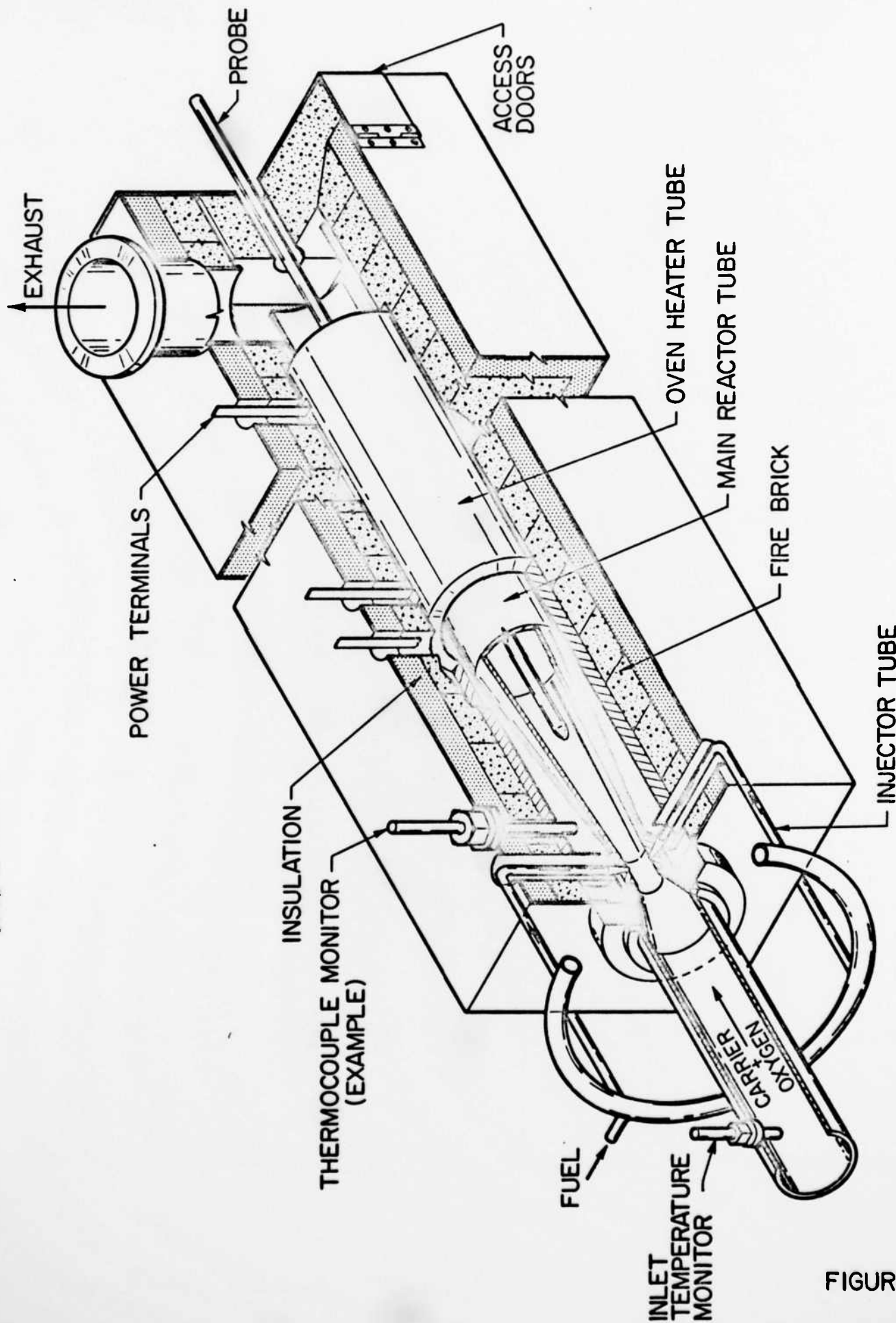
This research was supported by the Air Force Office of Scientific Research under Princeton University Grant AFOSR-74-2604 with Capt. Lloyd R. Lawrence, Jr., as technical monitor. This support is gratefully acknowledged.

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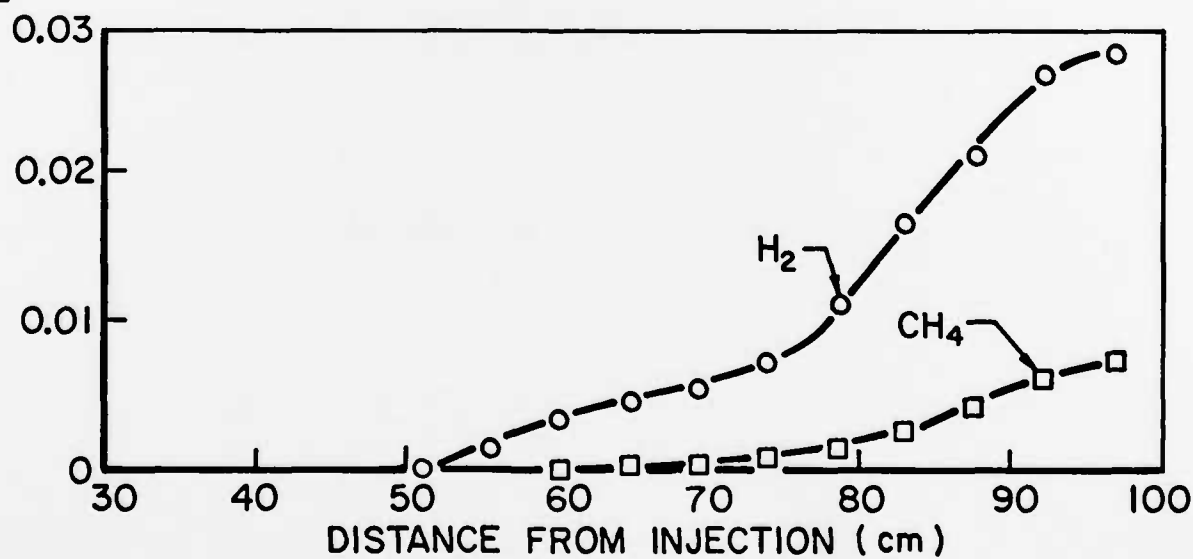
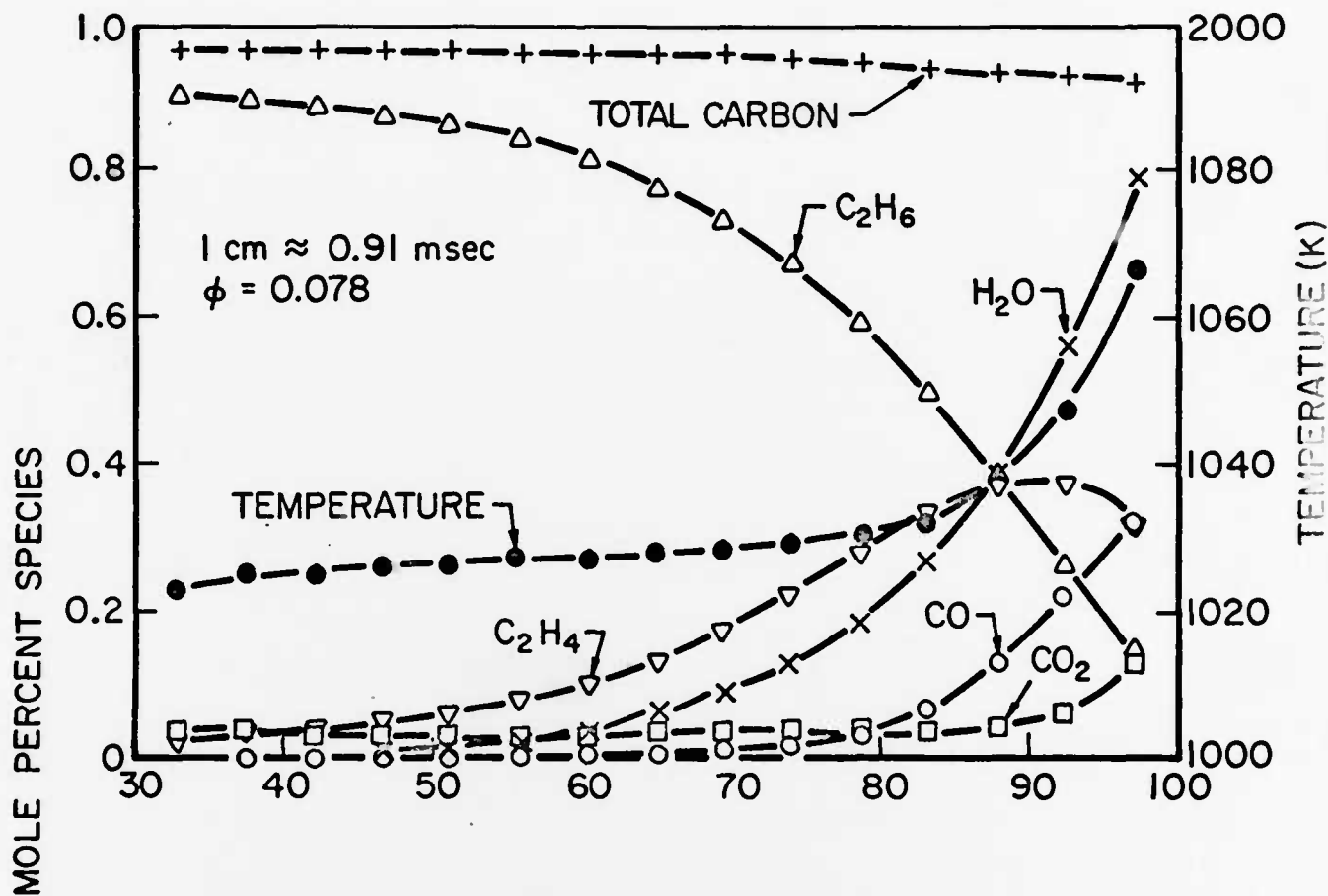
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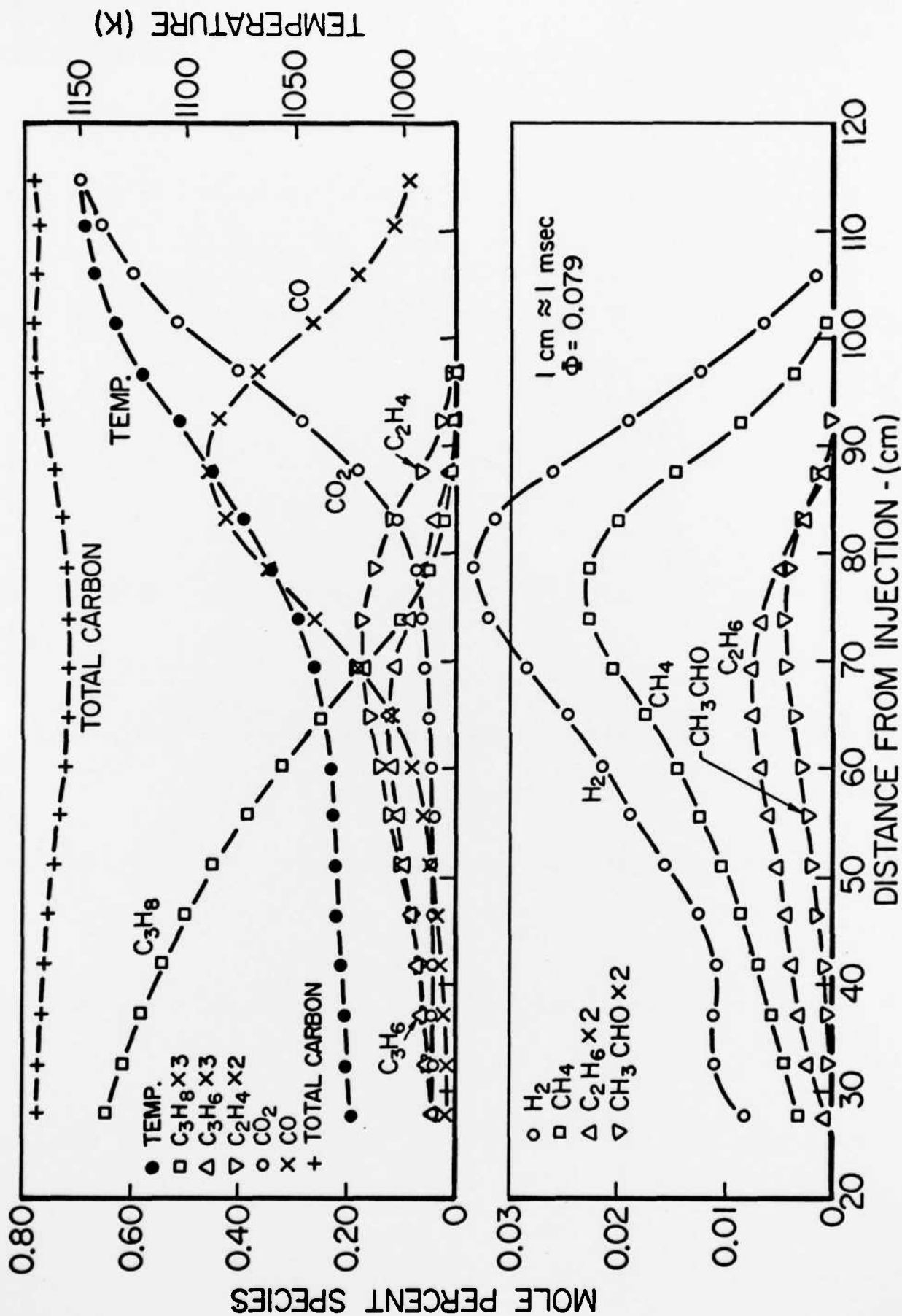
REACTOR ASSEMBLY

FIGURE I



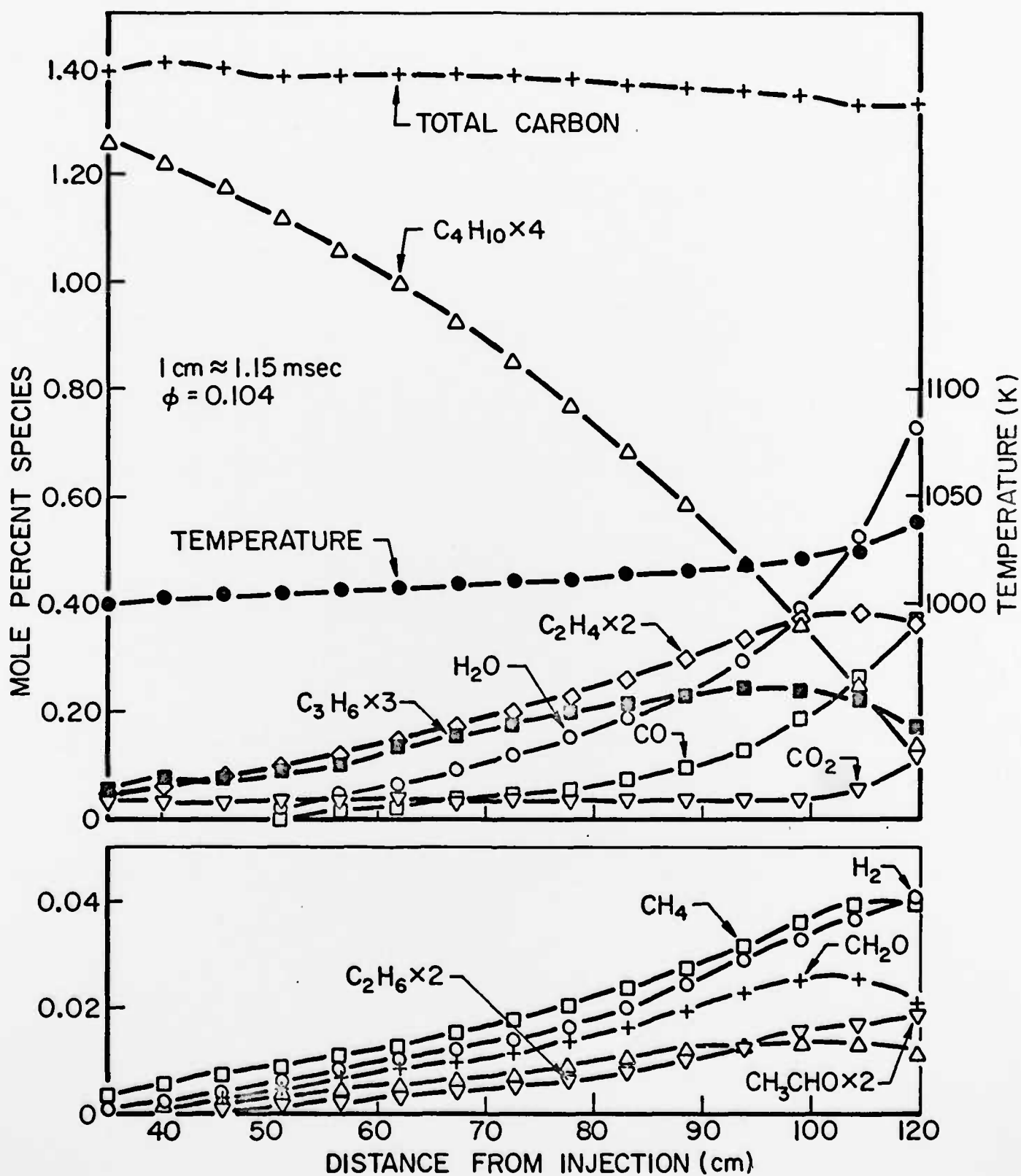
CHEMICAL COMPOSITION OF SPREAD
ETHANE-AIR REACTION

FIGURE 2



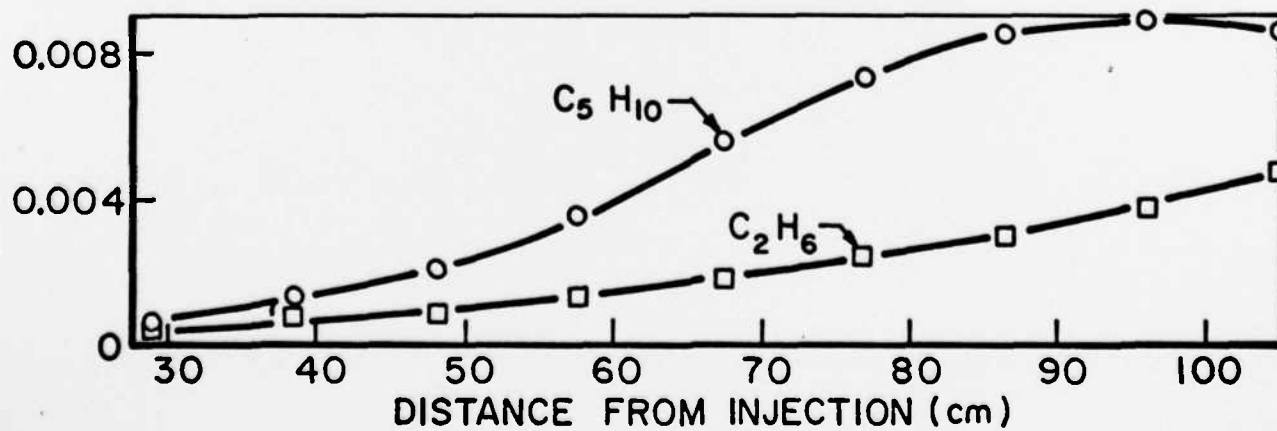
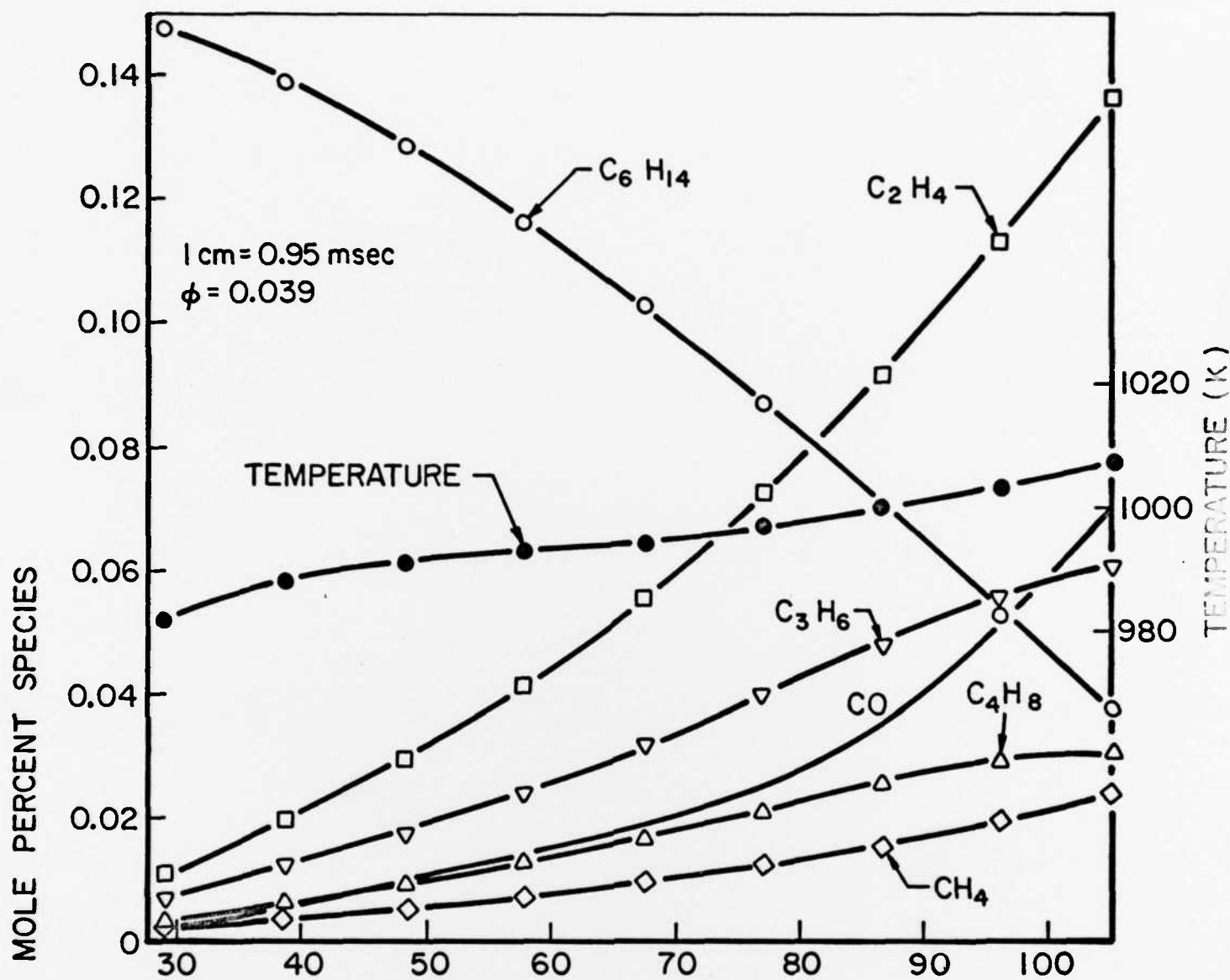
CHEMICAL COMPOSITION OF SPREAD PROPANE - AIR REACTION

FIGURE 3



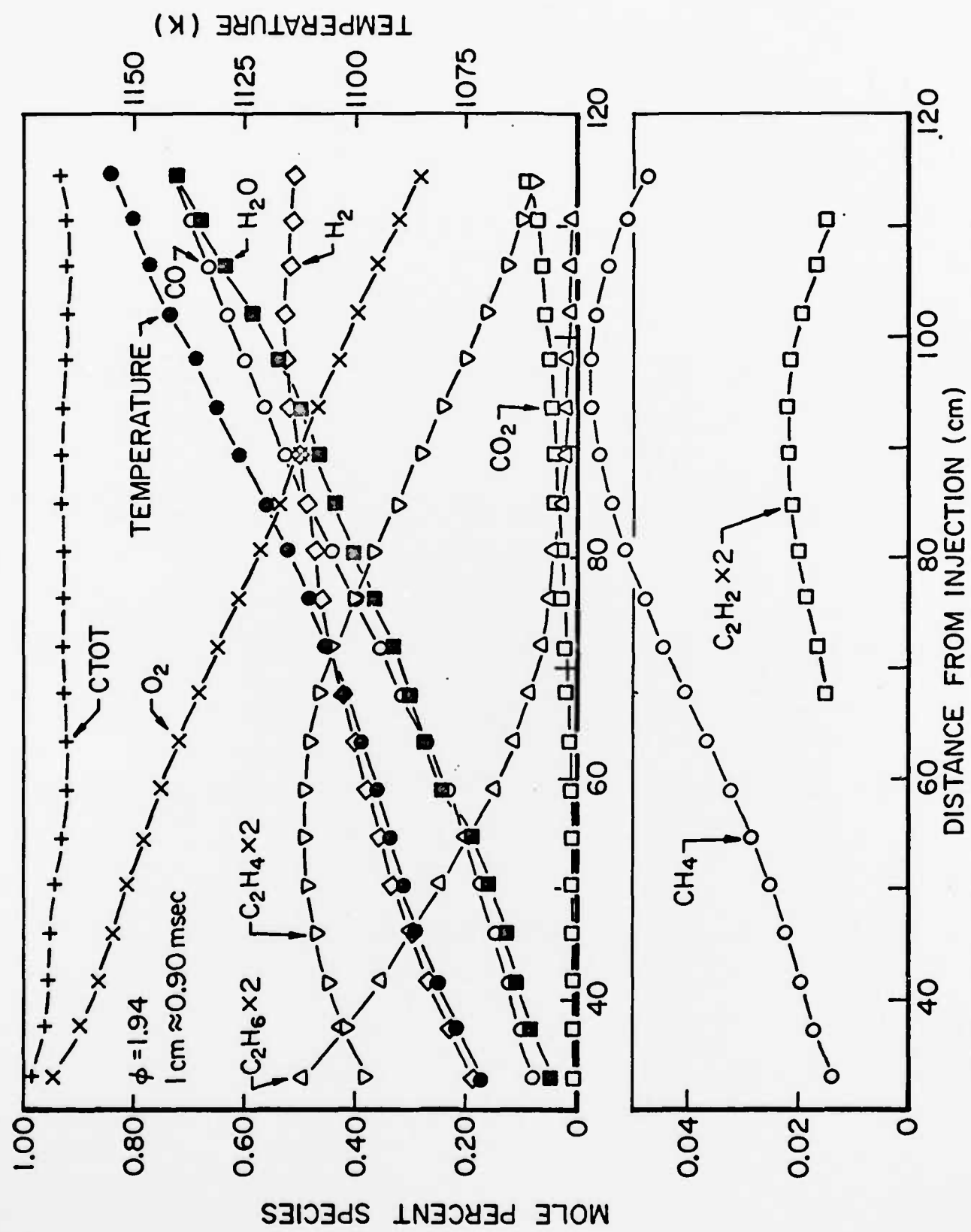
CHEMICAL COMPOSITION OF SPREAD
 BUTANE-AIR REACTION

FIGURE 4



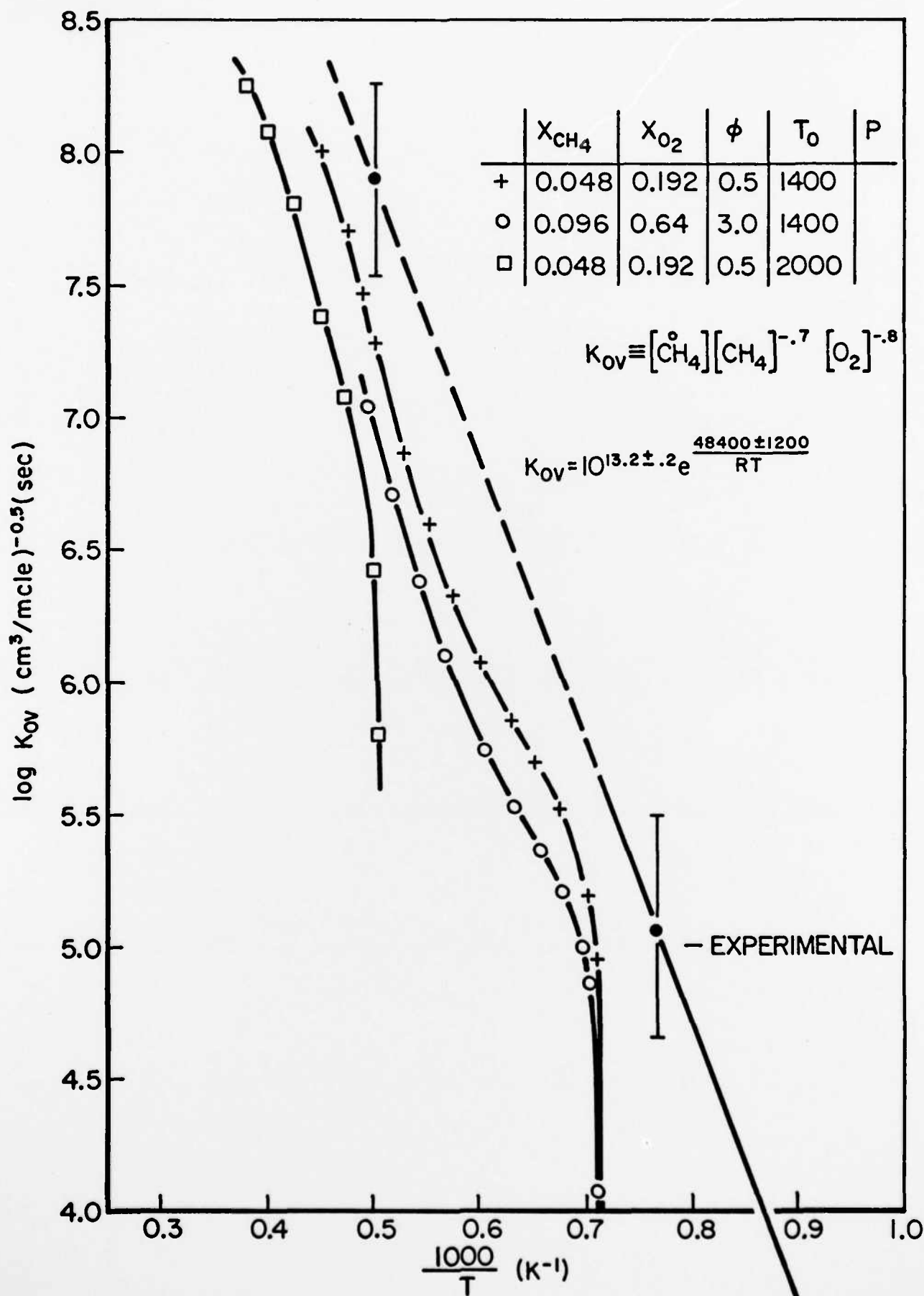
CHEMICAL COMPOSITION OF SPREAD
 HEXANE/AIR REACTION

FIGURE 5

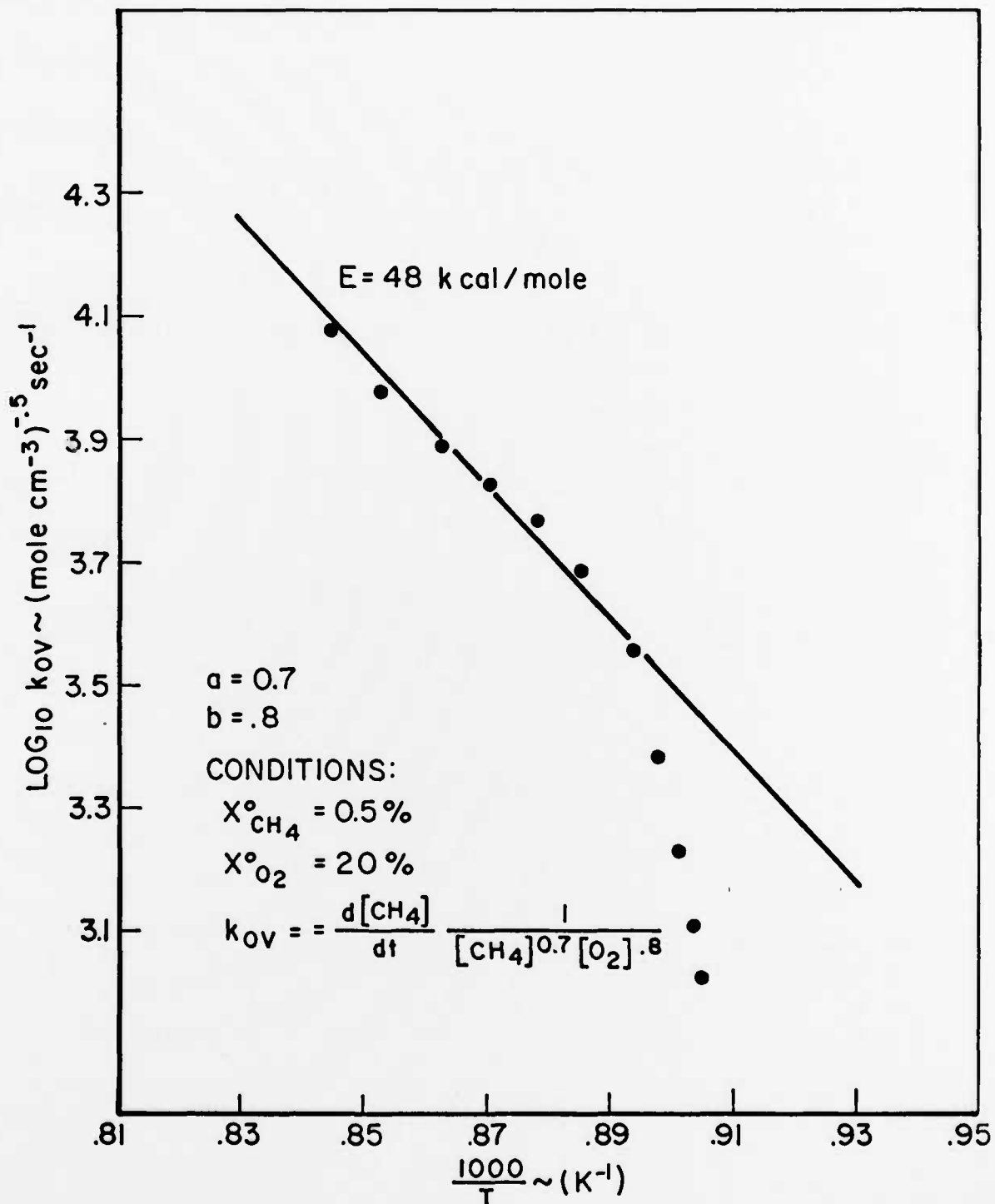


CHEMICAL COMPOSITION OF SPREAD ETHANE- O₂ REACTION

FIGURE 6

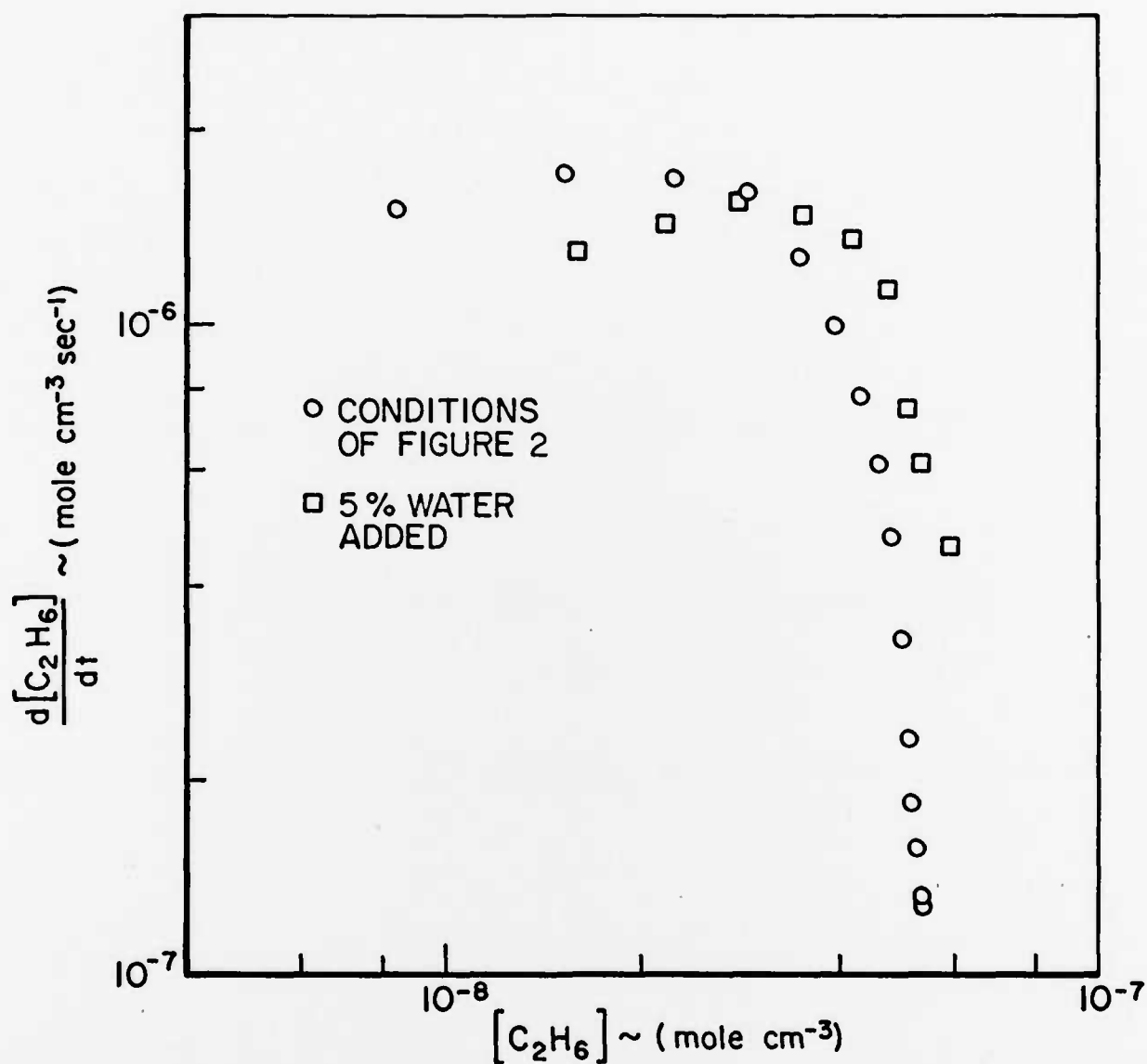


COMPARISON OF ANALYTICAL AND EXPERIMENTAL
OVERALL DISAPPEARANCE RATE OF METHANE



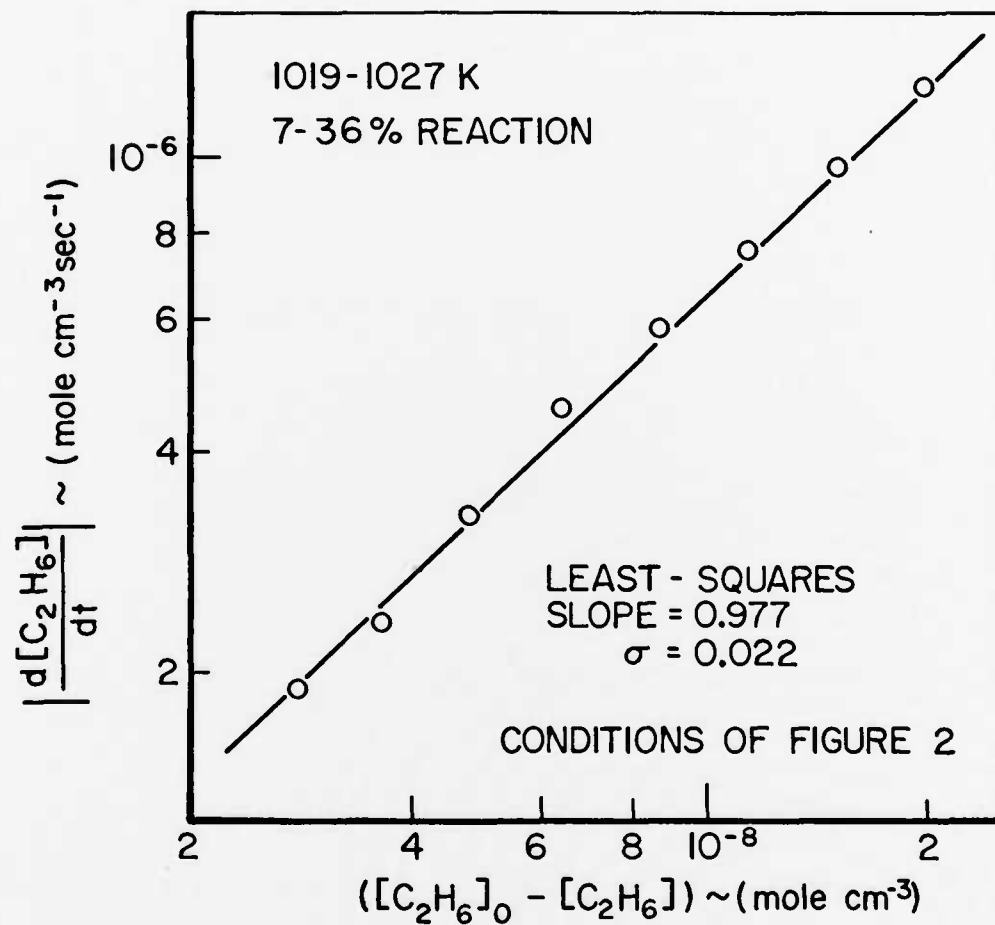
DETERMINATION OF E FOR REACTION OF CH_4/O_2

FIGURE 8



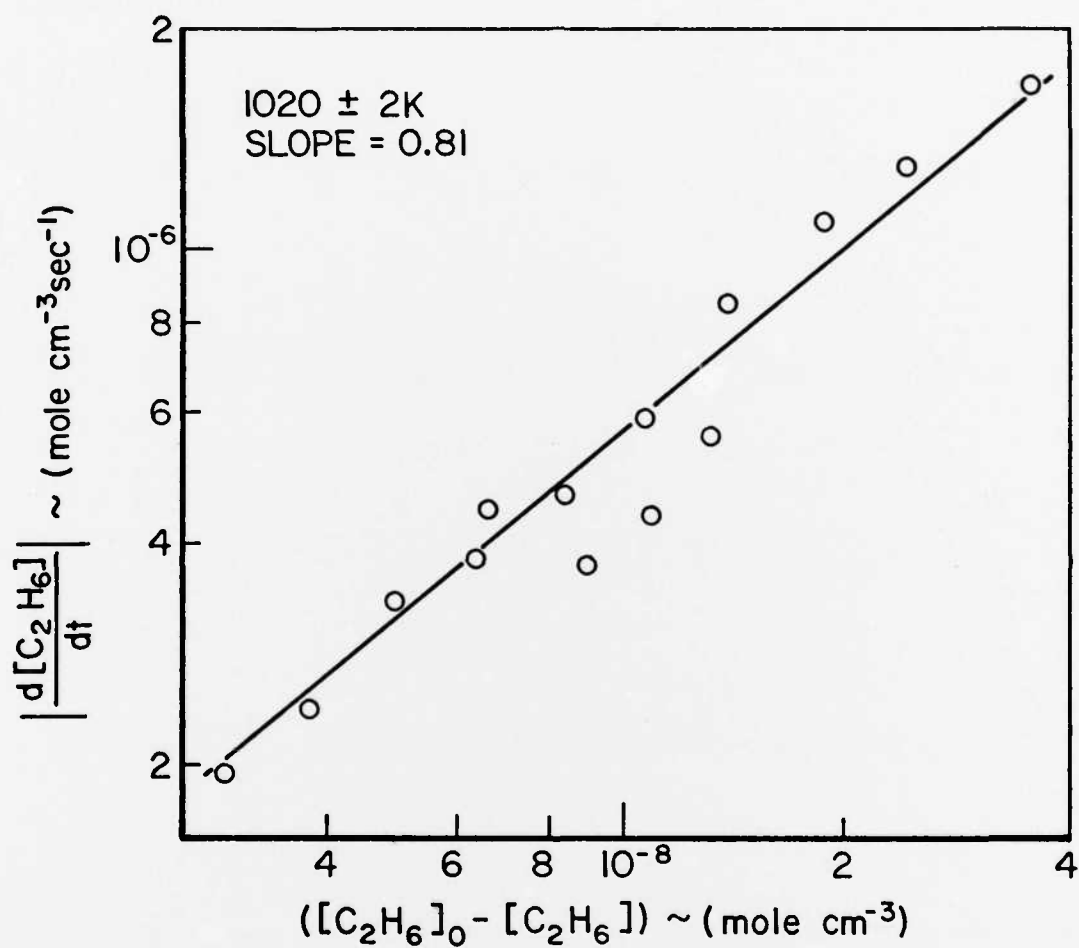
RELATION OF ETHANE DISAPPEARANCE RATE
ON ETHANE CONCENTRATION

FIGURE 9



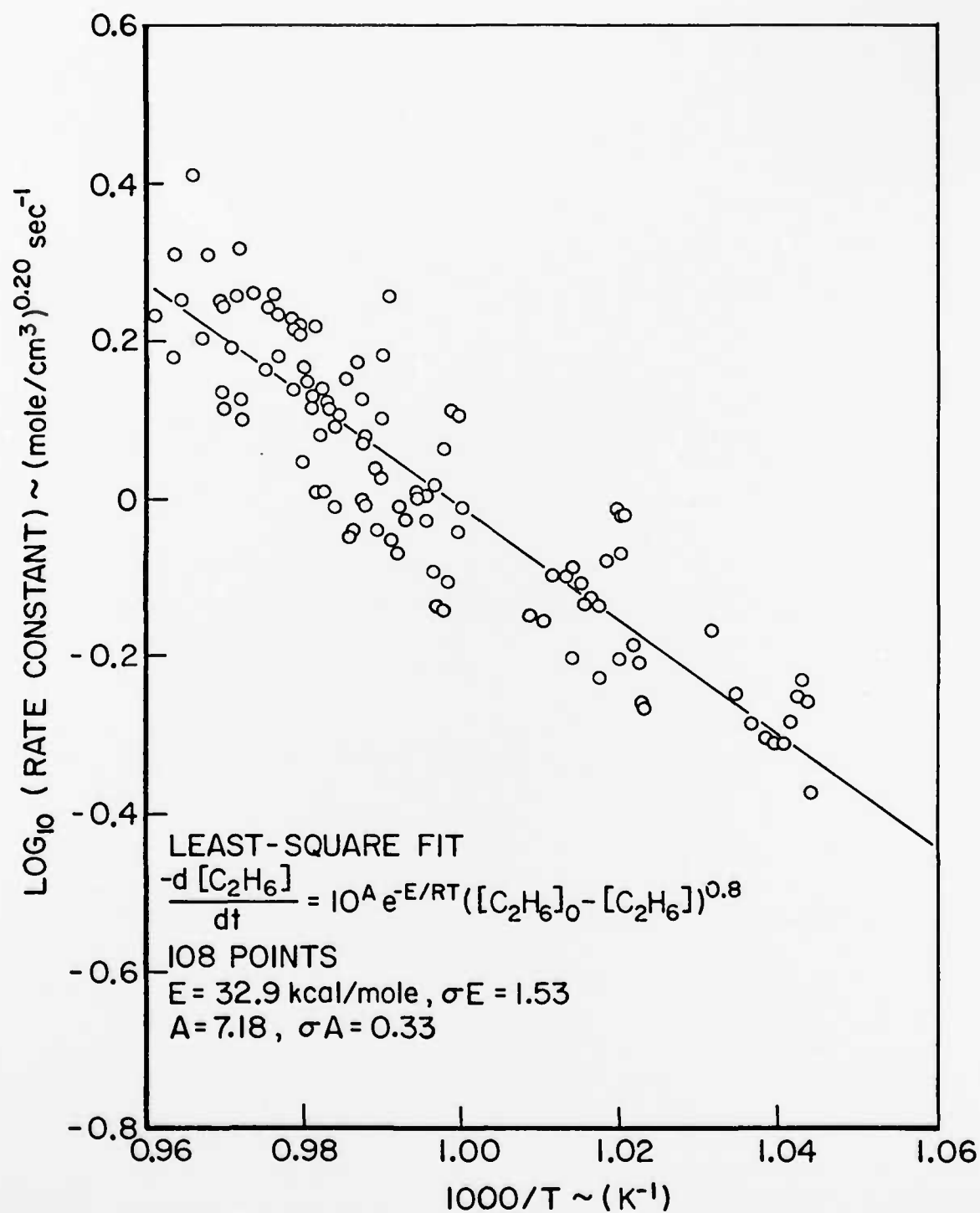
DEPENDENCE OF REACTION
RATE ON EXTENT OF REACTION

FIGURE 10



DEPENDENCE OF REACTION RATE
ON EXTENT OF REACTION

FIGURE 11



ETHANE/OXYGEN OVERALL REACTION RATE
 INDUCTION REGION
 950 - 1050K

FIGURE 12

END

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